

**A MAJOR ADVANCE IN POWDER METALLURGY**

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**ABSTRACT**

Under SBIR funding from the Army Materials Technology Laboratory, Ultramet has developed a process which promises to significantly increase the mechanical properties of powder metallurgy (PM) parts. Current PM technology utilizes mixed powders of various constituents prior to compaction. The homogeneity and flaw distribution in PM parts depends on the uniformity of mixing and the maintenance of uniformity during compaction. Conventional PM fabrication processes typically result in non-uniform distribution of the matrix, flaw generation due to particle-particle contact when one of the constituents is a brittle material, and grain growth caused by high-temperature, long-duration compaction processes. Additionally, a significant amount of matrix material is usually necessary to fill voids and create 100% dense parts. In Ultramet's process, each individual particle is coated with the matrix material, and compaction is performed by solid state processing. In the AMTL program, Ultramet coated 12-micron tungsten particles with approximately 5 wt% nickel/iron. After compaction, flexure strengths were measured 50% higher than those achieved in conventional liquid phase sintered parts (10 wt% Ni/Fe). This paper presents further results of the AMTL program and discusses other material combinations.

**INTRODUCTION**

Standard powder metallurgy techniques rely on the physical mixing of powder constituents in order to provide a homogeneous composite or alloy. Many approaches have been developed to permit better mixing, often focusing on reducing particle size: the smaller the size, the lesser the adverse effects of any isolated areas of nonhomogeneity. Small particles, however, lead to other problems such as increased surface area, which promotes greater reactivity with any embrittling impurities that are present. Also, fabrication costs are higher due to the difficulties encountered in handling fine particulates.

Ultramet's Army-sponsored research takes a different approach to promoting homogeneity. Through the use of chemical vapor deposition (CVD), Ultramet has demonstrated the capability of coating individual tungsten particles (5 to 20 microns in diameter) with varying levels of nickel, iron, cobalt, and combinations of the three. This method of "premixing" the composite constituents, exceeds by far the current capabilities of powder metallurgy, as the distribution of the matrix material is accomplished at the individual powder particle level. The ductility of metallic powder is ultimately enhanced, a highly desirable property for many applications.

**BACKGROUND****Chemical Vapor Deposition (CVD)**

CVD is a coating method that utilizes the decomposition of a gaseous precursor, flowed over or through a heated substrate, with subsequent condensation from the vapor state to form a solid deposit. The CVD process is an extremely versatile and relatively inexpensive method of molecular forming. Its benefits include the potential to produce deposits of controlled density, thickness, and composition, with extremely low impurity levels.

CVD has been successfully utilized for coating particles, including the production of ultrapure tungsten and niobium spheroids for metallurgical purposes and cladding of nuclear fuel (UO<sub>2</sub>) particles. As such, it represents a proven

approach with a large payoff. CVD has been used for the deposition of some 400 species, the processes for many of which were pioneered by Ultramet personnel.

The CVD process itself promotes greater purity, particularly for powder coating, as *in situ* gettering of contaminants can be performed in order to purify both the as-received (uncoated) powder and the resultant coatings. Also, the ability of CVD to produce multilayered or alloyed coatings allows for precise control of the desired physical and chemical characteristics of the final fabricated shape.

### Fluidized-Bed CVD

In order to uniformly coat fine particulates, fluidized-bed technology has been used. A schematic of a typical fluidized-bed CVD reactor, used for coating particles, is shown in Figure 1. The reactant gas stream is united with the powder fluidization gas just prior to entering the reactor. The metal precursor then preferentially decomposes on the surface of suspended powder particles entering the heated reaction zone, which act as nucleation sites for continuous film growth.

The gas flow in the entrance orifice must be greater than the terminal velocity of the particles so that particles do not fall down the orifice, and the gas velocity in the parallel section above the orifice must be less than the terminal velocity of the particles so that they are not blown out of the coater. In order to fluidize the particles, the gas velocity in the parallel section must be greater than the minimum fluidization velocity,  $u_{mf}$ , which is given by

$$u_{mf} = \frac{d_p^2(\rho_s - \rho_f)G}{1650\mu} \quad \left(\text{for } \frac{du\rho_f}{\mu} < 20\right) \quad (1)$$

where  $d_p$  is the particle diameter,  $\rho_s$  is the density of solids,  $\rho_f$  is the fluid density,  $G$  is the acceleration of gravity,  $\mu$  is the gas viscosity, and  $u_o$  is the superficial gas velocity.

The reactor shown in Figure 1 was designed to remove powder fines in order to produce an extremely narrow particle size distribution. The lighter fines are carried by the fluidizing gas stream into the disentrainment section, where they settle. Part of the proposed effort is aimed at developing scaling relations to translate the process to different particle sizes and densities.

Ultramet has developed a CVD fluidized-bed reactor capable of both fluidizing and coating metallic and ceramic particles as small as 5  $\mu\text{m}$  in diameter with a large number of different metal and ceramic materials. Efficient fluidization was previously limited to  $>15\text{-}\mu\text{m}$  particle diameters. The reduced size now available increases the driving force in sintering, since the sintering rate is roughly proportional to the inverse of the particle size. The resultant improved densification is a result of several concurrent processes. Smaller particle size leads to an increase in the energy associated with solid/pore interfacial areas, increasing the driving force available for compaction. Also, the greater interparticle contact provides more paths for volume diffusion or material transport, and the greater surface area allows for an increase in grain boundary/surface diffusion.

Powder particles are coated free of agglomeration, while the concentration and thickness of the deposited coating can be easily controlled. Standard powder metallurgy techniques involving powder mixing often lead to increased porosity and elemental heterogeneity. The use of prealloyed (uncoated) matrix powder particles eliminates the problem of heterogeneity, but these powders are very hard and compaction is difficult. At normal compaction pressures, the plastic deformation needed to obtain the amount of interfacial contact necessary for effective diffusion is difficult, and porosity results. The use of composite (coated) powders eliminates heterogeneity, allowing for a level of compaction comparable to or better than that available from elemental powders.

One of the primary advantages of CVD over most plating methods is the extremely high level of purity which may be obtained in the deposit. The majority of impurities in a coated powder batch is due to contamination in the as-received, uncoated substrate powder itself. In the case of deposition on tungsten powder, Ultramet has shown that light-element impurity levels (especially carbon and oxygen) may be substantially reduced through heat treatment, hydrogen reduction, and/or controlled water vapor treatment of the as-received tungsten powder. Carbon levels

were reduced by a factor of twelve from the as-received, uncoated powder to the coated, treated powder, and oxygen levels were reduced by a factor of four. Reduction of embrittling impurities leads to a substantial increase in mechanical properties.

## EXPERIMENTAL APPROACH

Ultramet's Army-sponsored research initially developed the capability to coat 12-micron tungsten particles with nickel, iron, and nickel/iron and nickel/cobalt mixtures via fluidized-bed chemical vapor deposition. Test specimens were then fabricated by densifying the coated tungsten particles via various consolidation methods; their microstructures were characterized; and their mechanical properties were measured at both quasistatic and elevated strain rates. Consolidation and testing focused on a (nominal) composition of 95 wt% tungsten/5 wt% nickel-iron, with the Ni:Fe ratio being 70:30 (overall composition 95W:3.5Ni:1.5Fe).

### Fabrication/Consolidation Technologies

Three fabrication/consolidation technologies were evaluated during the course of this work: liquid phase sintering (LPS), the Ceracon process, and hot isostatic pressing (HIP).

LPS was performed by AMTL as a baseline consolidation technology. The Ceracon process (Ceracon Inc., Sacramento, CA), a derivative of HIP involving dynamic force that induces compaction by both physical and activated sintering means, yielded encouraging results. HIP consolidation was performed by IMT (Portland, OR) on coated powders contained in evacuated stainless steel cans. Consolidation conditions (pressures, temperatures, times) for these methods are shown in Table I. A comparison between the microstructures obtained by Ceracon consolidation of Ultramet coated powder, and standard liquid phase sintering of mixed powders, is shown in Figures 2A and 2B. The uniformity of matrix dispersion in the Ultramet/Ceracon material is clearly evident.

### Mechanical Test Specimen Preparation

Three-point flexure testing was chosen to evaluate both strength and ductility by measuring midspan deflection and maximum flexural stress. Specimen dimensions were determined from the consolidated billet size available; therefore, the data shown should be used only to draw general conclusions about the various materials tested. Specimen dimensions are listed in Table I for all samples tested.

Three forms of consolidated W/Ni-Fe composite materials were tested: a commercial LPS material, a HIP material, and a Ceracon-consolidated material. The HIP and Ceracon processes utilized W:3.5Ni:1.5Fe powder that was fabricated by CVD at Ultramet. The LPS material was W:7.0Ni:3.0Fe, which was provided by AMTL in the form of an unworked, quarter-scale penetrator. The specimens were tested at ambient temperature using a cross-head speed of 0.25 mm/min (0.010"/min).

Hopkinson bar compression testing was performed at the University of California at San Diego (UCSD). Hopkinson bar specimens were 3.8-5.1 mm (0.150-0.200") diameter x 4.0 mm (0.156") long (the dimensions varying according to the size of the billet available).

## RESULTS AND DISCUSSION

Hopkinson bar compression test data, produced at UCSD, showed true strains of approximately 28% for 3900/sec and 4000/sec strain rates, and 76% for a 5000/sec strain rate. Engineering strains were  $\approx 22\%$  for the lower strain rate and 53% for the higher strain rate, indicating the presence of some elastic recovery in these composites.

Table I shows the results of flexure testing, including specimen size and composition, processing conditions, and midspan deflection (an indication of ductility). Figures 3A-3D show the results of metallographic analysis performed on HIP, LPS, and Ceracon consolidated materials. The consolidation conditions required to achieve 100% theoretical density via HIP were 1185°C (2165°F), 172 MPa (25 ksi), and 4.0 hours. The resultant microstructure (Figure 3A) exhibited substantial contact between tungsten particles and poor matrix distribution; no

attempt was made to optimize the HIP cycle. The 5% matrix HIP material exhibited ultimate stresses that were comparable to the 10% matrix LPS material (Figure 3B); however, the LPS material exhibited a greater midspan deflection. The processing conditions for the LPS material were much more complex, involving oxide reduction treatment before sintering, sintering at 1760°C (3200°F), and by a vacuum degas treatment. Sintering time is typically 30 min for a simple quarter-scale penetrator shape.

The most favorable combination of strength and deflection was exhibited by the 6% matrix material consolidated through the Ceracon process (Figure 3C). Consolidation conditions were 1235°C (2255°F), 1379 MPa (200 ksi), and 30 sec. This 6% matrix material exhibited strengths and midspan deflections over 50% greater than those of the 10% matrix commercial material. Figure 4 is a photograph of a W:4.5Ni:1.5Fe flexure test bar, showing an unusual degree of bending for such a tungsten-heavy material.

The differences in mechanical behavior may be explained by the homogeneity of matrix distribution, which was a primary goal of this work: to demonstrate that improving the matrix dispersion over standard PM techniques will improve physical properties as well. The SEM micrographs of these materials (Figures 3A, 3B, and 3C) support this hypothesis.

The Ultramet CVD/HIP material (Figure 3A) exhibited an almost entirely intergranular fracture mode. The sharp-edged, faceted fracture surfaces resulted from the brittle fracture behavior that is expected at the interface of tungsten grains in direct contact. The matrix material, initially designed to provide an interface between tungsten grains, was extruded into triple point locations between grains. These high matrix content areas are clearly evident in the micrographs. In addition, a portion of the intergranular fracture most likely involved the breaking up of the several tungsten single crystals that made up each tungsten grain, prior to CVD coating.

The commercial LPS material (Figure 3B) exhibited fracture in virtually a single plane of tungsten particles. The flat areas shown on individual tungsten grains were interfaces between tungsten particles with no matrix material present. Figure 3D, meanwhile, clearly shows the bright tungsten flat areas on individual tungsten grains, with no sign of the Ni-Fe matrix material. The result was again predominantly intergranular failure.

The material fabricated through the Ultramet CVD/Ceracon process (Figure 3C) exhibited fracture behavior that was significantly different from the other two materials. There was evidence of three different failure modes: intergranular, intragranular, and grain pullout. The latter was different from that shown in the HIP sample, in that the void left from the removed grain was lined with Ni-Fe matrix material. The high transverse rupture strength is attributed to the low incidence of tungsten-tungsten particle contact.

## COMMERCIAL APPLICATIONS

Ultramet has demonstrated the ability to coat individual powder particles by CVD, forming a true "composite" metal by the integration of a hard metal powder reinforcing phase with a ductile matrix. The expected improvements in mechanical properties are thought to be due to a nearly perfect distribution of matrix material about the individual tungsten particles in a 95 wt% tungsten composite. Table II shows the various powder/coating combinations that have been successfully obtained at Ultramet.

The combined new technologies developed in this work will mitigate or remove the present barriers to improving powder metallurgy component fabrication. The result will be components with dependably better properties and narrower, more predictable statistical property distributions. The size and weight of load-bearing sections of components can be reduced without giving up strength, or strength can be increased without increasing size and weight. A narrow, more predictable statistical variation in mechanical properties provides more confidence in designing structures utilizing such new materials.

The military applications of this technology are obvious. The DARPA armor/antiarmor initiative has identified advanced kinetic energy weapons as an area where major improvements in U.S. capabilities are needed. The application of new, innovative powder preparation and consolidation technologies will reduce costs and provide the performance improvements necessary to penetrate present and future armor.

Improved ductility and densification of materials for penetrator devices is only one of the possible applications of this technology. In addition to ordnance applications, tungsten heavy metal alloys have utility in neutron shielding. Better mechanical properties and homogeneity may allow improvement in the performance/weight consideration for such applications. Graded seals and conductive ceramics are also areas of interest.

Ultramet's powder coating technology has many more subtle, but potentially very important, benefits to both government and commercial interests. Powder metallurgy recently has made great strides in the fabrication of difficult-to-process alloys, including metastable structures for increased wear and corrosion resistance as well as stronger alloys to permit weight reduction. The latter is of great interest to many military systems, among them helicopters, fighter aircraft, ground vehicles, and artillery.

Prospects are also very good for making use of this technology in the fabrication of cemented carbide tools and wear parts, currently a \$1 billion market. It is likely that these tools' transverse rupture strength and impact strength can be measurably improved. Ultimately, the entire area of metal/ceramic composites will be impacted by this technology. One example of such an advanced composite is ceramic-strengthened intermetallic materials for use in aerospace engines and structures.

While this effort has focused on the development of improved powders for tungsten heavy metal composites, this technology is being extended to develop a wide range of powder compositions for the metals, ceramics, and composites industries. Compositions and applications ready for immediate development include:

- Custom-coated powders for plasma spraying.
- Ceramic powders integrally coated with their corresponding sintering aids. Like the tungsten composites, this leads to reduced sintering times and temperatures, reduced grain growth, reduced contamination, and improved properties and economics.
- Matrix-coated silicon carbide (SiC), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), boron carbide ( $\text{B}_4\text{C}$ ), cubic boron nitride (CBN), diamond, and other powders leading to improved cutting tool performance and improved plasma-sprayed wear-resistant coatings.
- Matrix- and/or interface-coated whiskers and particulates leading to injection-moldable, more cost-effective composites.
- Extension of mechanical alloying technology to include interstitial-sensitive metals such as titanium and niobium. The mating of CVD and mechanical alloying theoretically allows almost any combination of materials to be fabricated in a dispersion-strengthened composite.
- Diffusion barrier/compatibility layer coating of microspheres, powders, and particulates providing wetting and stability of fillers and reinforcements. Potential applications include stabilizing filler particle oxidation state for high temperature magnetic and electronic applications, modifying the bonding and long-term stability of SiC whiskers in titanium alloys, among others.

#### ACKNOWLEDGMENTS

This work was performed under contract #DAAL04-88-C-0030 with the Army Materials Technology Laboratory (Watertown, MA). The Ultramet authors would like to thank the AMTL program managers, Dr. Kenneth J. Tauer and Robert J. Dowding, for their support and assistance throughout the performance of this work, and Dr. Ramas V. Raman and Sundeep Rele at Ceracon for their expert advice and assistance in powder consolidation.

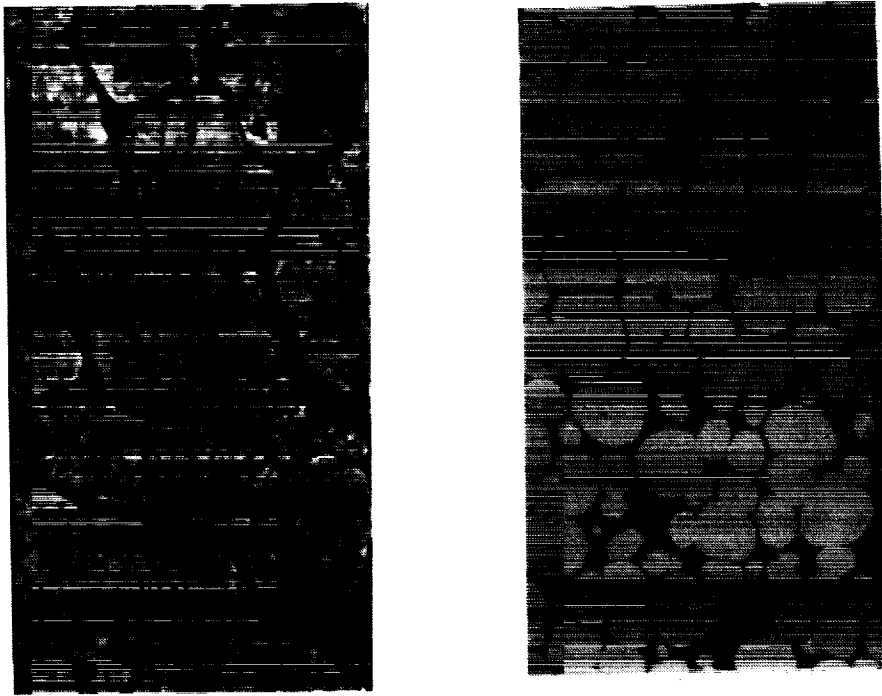


Figure 2. A (top): SEM micrograph of Ultramet W:3.5Ni:1.5Fe material consolidated by Ceracon, showing extreme uniformity of matrix dispersion (2000x) B (bottom): SEM micrograph of AMTL W:3.2Ni:1.0Fe material consolidated by LPS, showing extreme tungsten-tungsten particle contact and nonhomogeneous matrix dispersion (400x)

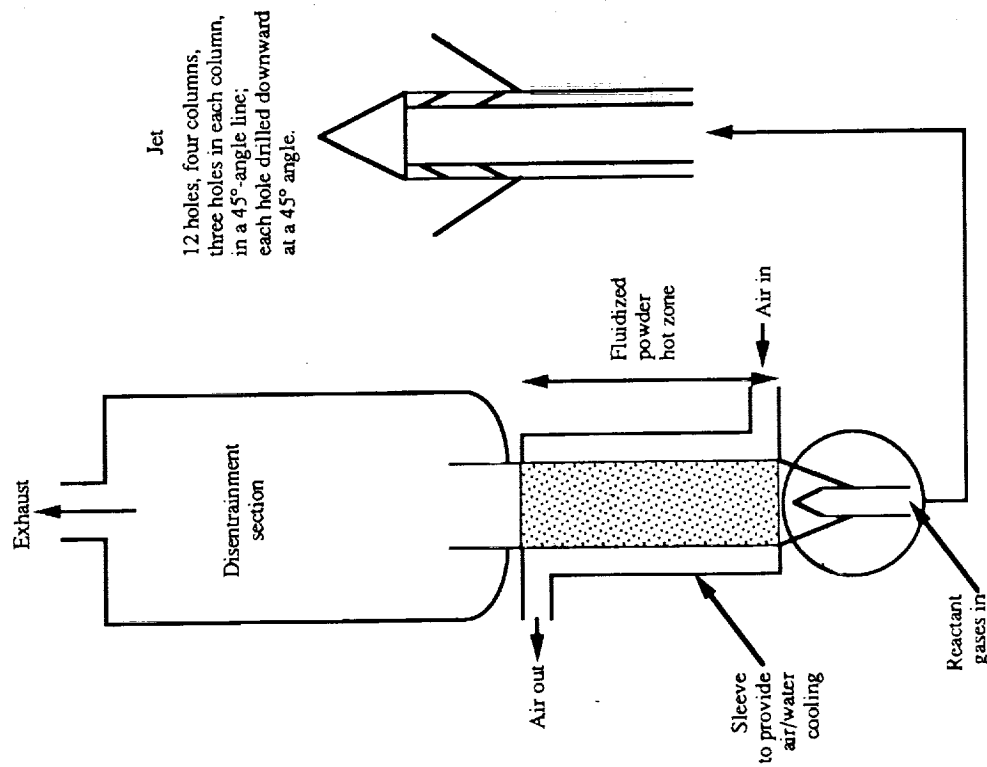


Figure 1. Schematic of fluidized-bed CVD apparatus

Table I. Flexure Test Results (Three-Point Loading)												
Length (in) (mm)	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29	0.5625 14.29
Width (in) (mm)	0.1903 4.834	0.1894 4.811	0.1894 4.811	0.1894 4.811	0.1860 4.724	0.1890 4.801	0.1890 4.801	0.1890 4.801	0.1488 3.780	0.1492 3.790	0.1494 3.795	0.1494 3.795
Depth (in) (mm)	0.1630 4.140	0.1590 4.039	0.1590 4.039	0.1590 4.039	0.1490 3.785	0.1500 3.810	0.1500 3.810	0.1500 3.810	0.1260 3.200	0.1255 3.188	0.1260 3.200	0.1260 3.200
Composition: %W %Ni %Fe % uncoated 5- $\mu$ m tungsten powder	95.3 3.5 1.2 10.0	95.3 3.5 1.2 10.0	95.3 3.5 1.2 10.0	95.3 3.5 1.2 10.0	90.0 7.0 3.0 0.0	90.0 7.0 3.0 0.0	90.0 7.0 3.0 0.0	90.0 7.0 3.0 0.0	94.0 4.3 1.7 0.0	94.0 4.3 1.7 0.0	94.0 4.3 1.7 0.0	94.0 4.3 1.7 0.0
Consolidation temp. ( $^{\circ}$ F) ( $^{\circ}$ C) pressure (ksi) (MPa) duration (hr)	HIP 2165 1185 25 172.4 4	HIP 2165 1185 25 172.4 4	HIP 2165 1185 25 172.4 4	HIP 2165 1185 25 172.4 4	LPS 2730 1500 n/a 1	LPS 2730 1500 n/a 1	LPS 2730 1500 n/a 1	LPS 2730 1500 n/a 1	Ceracon 2255 1235 200 1379 0.008	Ceracon 2255 1235 200 1379 0.008	Ceracon 2255 1235 200 1379 0.008	Ceracon 2255 1235 200 1379 0.008
Measured Density (g/cm <sup>3</sup> )	18.24	18.24	18.24	18.24	17.15	17.15	17.15	17.15	17.95	17.95	17.95	17.95
Theoretical Density (g/cm <sup>3</sup> )	18.24	18.24	18.24	18.24	17.15	17.15	17.15	17.15	17.95	17.95	17.95	17.95
Percent Dense	100	100	100	100	100	100	100	100	100	100	100	100
Deflection (in) (mm)	0.011 0.279	0.009 0.229	0.009 0.229	0.009 0.229	0.017 0.432	0.015 0.381	0.015 0.381	0.015 0.381	0.024 0.610	0.018 0.457	0.020 0.508	0.020 0.508
Maximum Load (lbf) (N)	1217 5413	1162 5169	1162 5169	1169 5200	1000 4448	1111 4942	1111 4942	1111 4942	889 3954	801 3563	785 3492	785 3492
Ultimate Stress (ksi) (MPa)	203 1400	205 1413	205 1413	206 1420	204 1407	220 1517	220 1517	220 1517	318 2193	288 1986	279 1924	279 1924

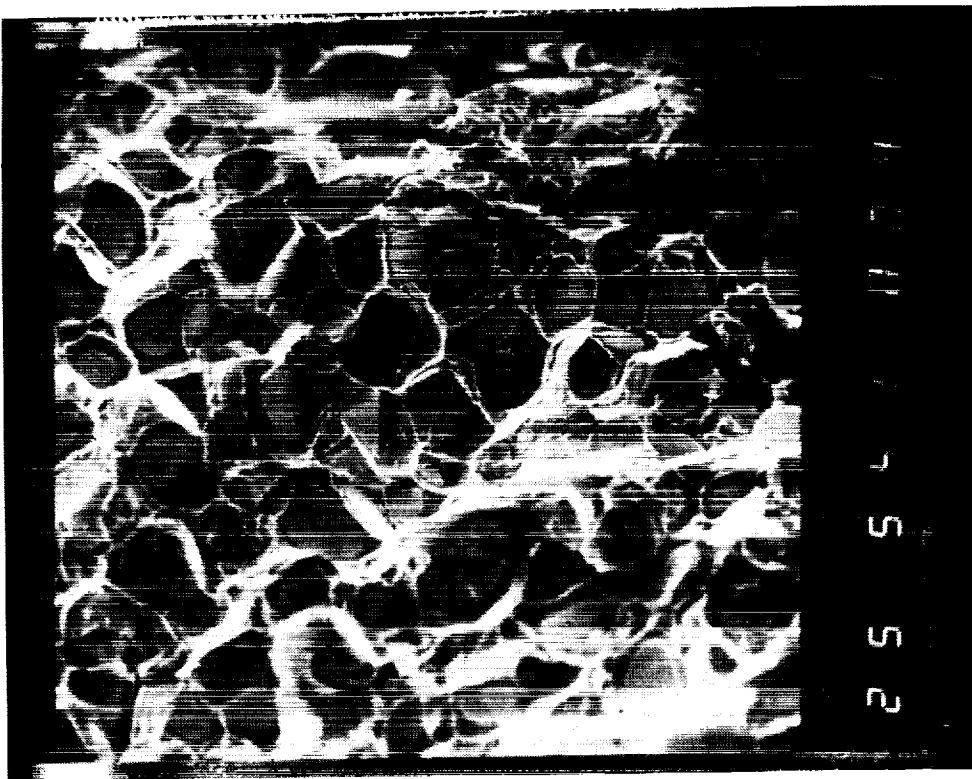


Figure 3B. SEM micrograph of W:7.0Ni:3.0Fe material consolidated by LPS (fracture surface, 540x), showing poor matrix dispersion leading to intergranular fracture originating at the flat surfaces seen on individual tungsten grains.



Figure 3A. SEM micrograph of W:3.5Ni:1.5Fe material consolidated by HIP (fracture surface, 2000x), showing poor matrix dispersion leading to intergranular fracture.



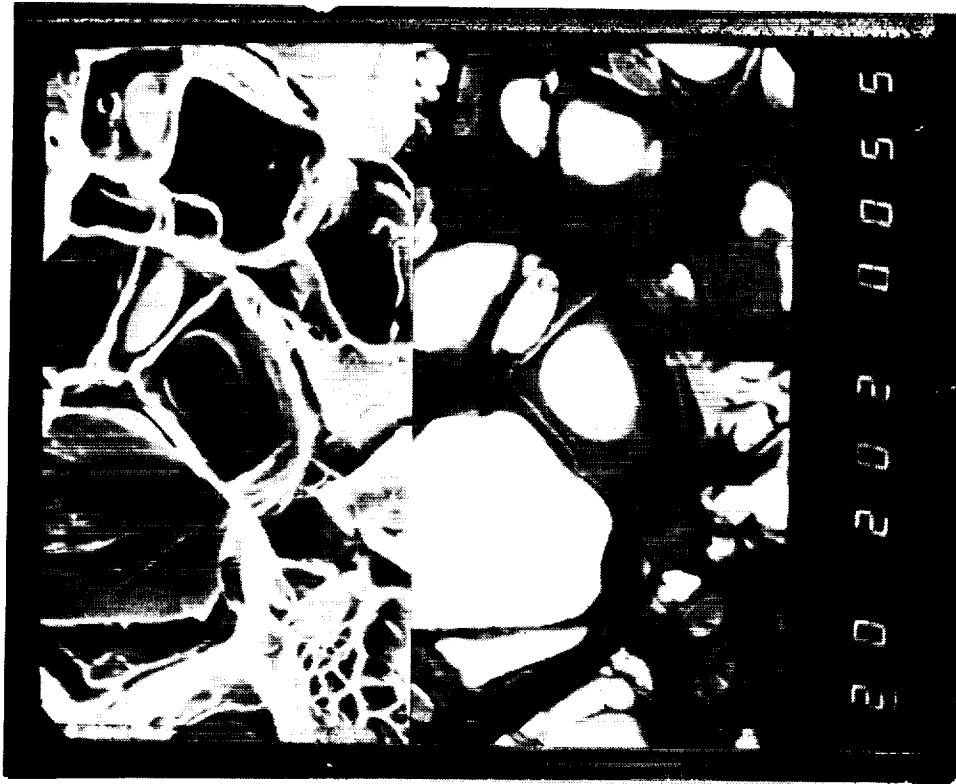


Figure 3D. SEM micrograph of W:7.0Ni:3.0Fe material consolidated by LPS (secondary [top] and backscattered [bottom] electron images, fracture surface, 2000x). The shiny flat surfaces on individual grains were areas of tungsten-tungsten particle contact prior to fracture; no sign of Ni-Fe matrix material is evident in these areas.

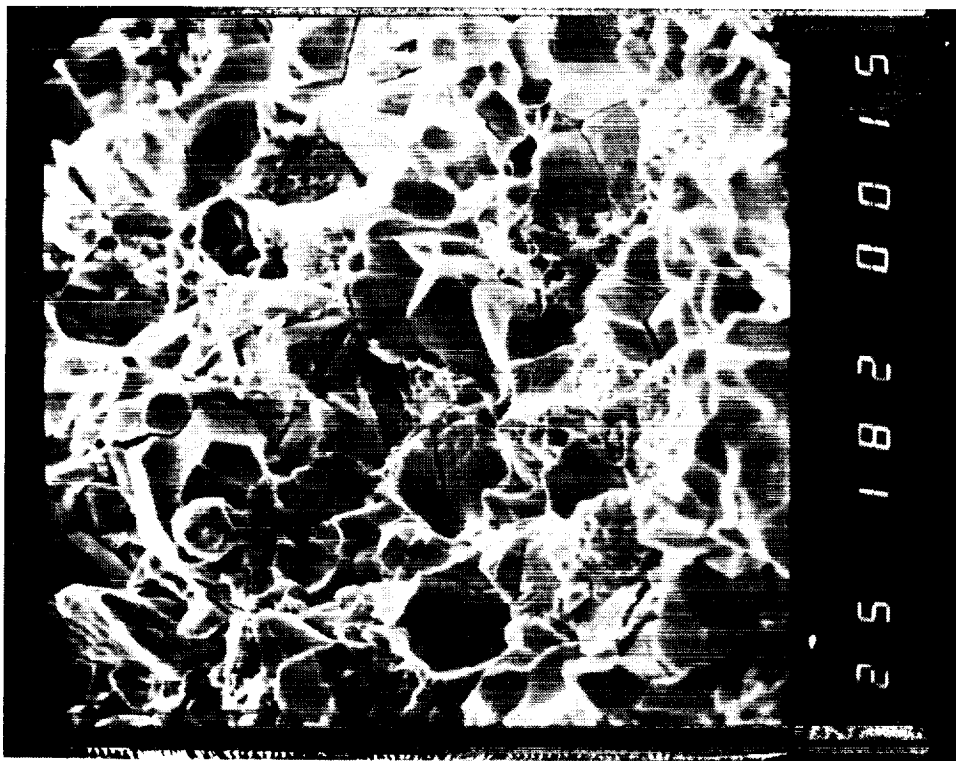


Figure 3C. SEM micrograph of W:3.5Ni:1.5Fe material consolidated by Ceracon (fracture surface, 1800x), showing significant intragranular failure and grain pullout in addition to intergranular fracture.

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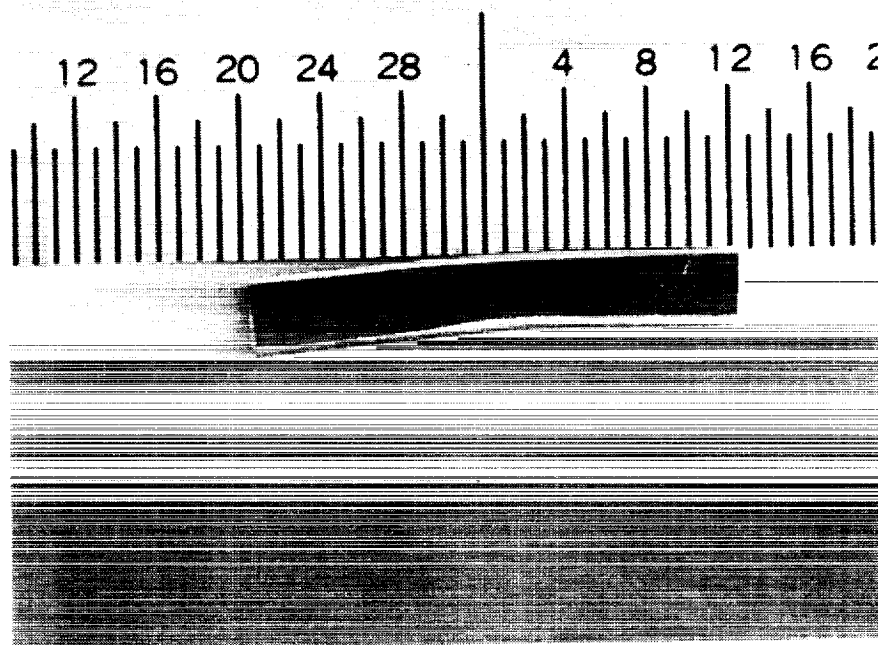


Figure 4. W:4.5Ni:1.5Fe composite flexural specimen following three-point loading test, which was aborted just prior to expected fracture in order to show degree of bending exhibited.

Table II. Powder Coating Programs at Ultramet

Description (coating on powder)	Application
3.5Ni:1.5Fe on 12- $\mu$ m tungsten	Ordnance
5-50 wt% copper on 100- $\mu$ m AlN	High conductivity composites
10-30 wt% aluminum on 5- $\mu$ m TiB <sub>2</sub>	Dispersion strengthening
TiB <sub>2</sub> on 5- $\mu$ m aluminum	Dispersion strengthening
80 wt% tungsten on 150- $\mu$ m Al <sub>2</sub> O <sub>3</sub>	Proprietary
10 wt% Al <sub>2</sub> O <sub>3</sub> on 100- $\mu$ m SiC	Ceramic composites
20 wt% titanium on 100- $\mu$ m Al <sub>2</sub> O <sub>3</sub>	Proprietary
5 wt% iron on 100- $\mu$ m WC	Cutting tools
3 wt% cobalt on 10- $\mu$ m WC	Cutting tools
3 wt% iron on 20-500- $\mu$ m diamond	Cutting tools
10-20 wt% hafnium and titanium on 12- $\mu$ m tungsten	Ordnance